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THE USE OF YOUNG'S MODULUS TO MONITOR RELAXATION IN METALLIC GL--ETC(U)
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THE USE OF YOUNG'S MODULUS TO MONITOR RELAXATION IN METALLIC GLASSES

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ABSTRACT

The kinetics of change of Young's modulus (E) during isothermal relaxation and crystallisation of an all-metal glass, $Cu_{60}Zr_{40}$ have been measured by a pulse-echo technique. E increases by about 10% between the as-quenched and fully relaxed states. Crystallisation of the glass produces a further 15% increase in E. The kinetics of the relaxation process can be fitted to an expression of the form $\Delta E = a \ln t + b$.

A glassy material, formed by quenching the appropriate liquid, is always metastable with respect to at least one crystalline phase. In addition, the glass in it's as-quenched state may be metastable with respect to the so-called "thermodynamically ideal" glass. This is particularly so in the case of metallic glasses where the very high quenching rates necessary for glass formation lead to a deviation from equilibrium at a fictive temperature T_f which is well above the thermodynamic glass transition temperature T_g. Consequently the physical properties of metallic glasses may depend to a large extent on the large excess free volume quenched into the glass. During subsequent annealing below T_g this excess free volume is either eliminated or redistributed leading to changes in magnetic, electrical and mechanical properties. One property which changes significantly is the Young's modulus (E); On heating to T_g and cooling to room temperature the modulus of a Pd-Cu-Si glass increases by about 7%; crystallisation of the same glass increases E by about 30% (3). During identical heat treatments the density of the glass increases by only 0.3% during relaxation and 1.5% on crystallisation (4). The large changes in Young's modulus, therefore, do not arise purely from densification but must be a consequence of either the rearrangement of defects within the glass or changes in chemical short range order. It appears to us that the Young's modulus might be a very sensitive monitor of the relaxation kinetics of metallic glasses. Unlike the magnetic measurements previously reported (5,6) such a technique would be applicable to all metallic glasses. In this letter we describe modulus measurements on the glass $Cu_{60}Zr_{40}$. To our knowledge this is the first time that such measurements have been used to study relaxation and crystallisation of a glass. Moreover apart from some earlier stress-relief measurements by one of us (7) it is the only study

of the relaxation kinetics of an all-metal glass.

Glassy ribbons of $Cu_{60}Zr_{40}$, 2mm wide and 25μm thick were produced by melt-spinning. The glassiness was verified by x-ray diffraction and differential scanning calorimetry. As will be described later some ribbons contained a small fraction of crystallinity. The Young's modulus (E) was determined from $E = \rho V^2$ where ρ is the density of the ribbons and V the velocity of 156 kHz extensional waves. A pulse-echo technique was used to measure V in ribbons 100 to 150 mm in length. The high resolution (10ns) of the system allowed determination of the delay time (τ) between the initial pulse and the first reflection to be measured to better than 1 part in 10^4. To minimise dispersion only specimens with well defined edges were used. The density of the as-quenched ribbons was measured by the Archimedean technique modified for small (30mg) specimens (8) and found to be 7.635 ± 0.005 gcm^{-3}. Errors in the density were therefore the largest inaccuracy in the absolute values of E. Changes in length of the ribbons during annealing were measured to better than 0.1% using a travelling microscope. However, as we shall show later, the contribution of change in density to change in Young's modulus (ΔE) was two orders of magnitude less than that of the change in wave velocity. Consequently, such density changes were ignored and all values of E were calculated from the density of the as-quenched glass. To monitor the change in modulus during heat treatment the ribbons were isothermally annealed in a specially designed tube furnace. By sandwiching the specimens in a pre-heated copper holder it was possible to give reliable anneals for times as short as 15s.

The ribbons were annealed successively and the Young's moduli measured at room temperature. In this manner the corrections for thermal expansion necessary in in-situ experiments were eliminated.

Fig. 1 shows the change in reduced delay time ($\tau_r = \tau/\tau_o$, where τ is the delay time for the as quenched ribbon) during annealing at various temperatures. At all temperatures the behaviour was the same; an initial rapid decrease was followed by a much slower rate of decrease which persisted for long times. The change in length during annealing was not a simple contraction but initial contraction followed by expansion. Overall the change in length was small (0.03 to 0.1% depending on temperature) and, as stated above, was ignored in the calculations of Young's modulus. During relaxation the change in Young's modulus was logarithmic in time i.e. it could be fitted to an expression of the type: $\Delta E(T,t) = a \ln t + b$ where a and b are constants which depend on the annealing temperature and initial sample condition (Fig. 2). This relationship held for all temperatures up to 770K and over a time scale as long as 3 days. By annealing at high temperatures e.g. at 500°C it was possible to fully relax the glass and obtain a "saturation" value for E. At 500°C this value was retained for about 90 sec before E rose sharply due to crystallisation. The incubation time for crystallisation measured in this way ($\sim$ 100 sec) agreed well with that determined at the same temperature by DSC ($\sim$ 150 sec). The Young's modulus of the crystallised sample was about 11% greater than that of the fully relaxed glass and about 20% greater than that of the as-quenched glass. The dashed curves in Fig. 2 show the behaviour of specimens known to contain a small percentage of crystallinity after quenching.

The behaviour was significantly different from the fully glassy specimens. At short times relaxation of E obeyed the log time relationship but at longer times E increased rapidly as the quenched-in crystals grew at the expense of the glassy matrix.

The kinetics of relaxation were, in form, identical to both those for stress relief measured in the same glass (7) and those measured by a variety of techniques during the relaxation of glasses of the transition metal-metalloid type (10). Such kinetics, which may be described by the general equation:

$$f(t,T) = A \ln \left(\frac{t}{t_o} + 1\right) \text{ where } A(t,T) \text{ is a constant}$$

have also been observed for creep recovery (11) and the annealing of radiation induced voids in aluminium (12). In both these cases the underlying physical mechanism is the depletion of an excess defect concentration and f(t,T) is the fraction of defects that has been annealed out. Damask and Dienes (13) have shown that in such cases the log time kinetics may arise from a first order reaction process:

$$\frac{df}{dt} = K_o (1-f) \exp - {}^{Q}/_{kt} \qquad [1]$$

where the activation energy Q is proportional to f, such that:

$$Q = \alpha f \qquad [2]$$

$$\text{i.e. } \frac{df}{dt} = K_o (1-f) \exp \frac{-\alpha f}{kT} \qquad [3]$$

Equation 3 can be solved in terms of exponential integrals to yield (9):

$$f = \frac{kT}{\alpha} \ln \left(\frac{t}{t_o} + 1\right) \qquad f << 1 \qquad [4]$$

where $t_o = \frac{kT}{c\alpha} \exp \frac{\alpha f_o}{kT}$

The nature of the structural defects in metallic glasses and their behaviour during annealing are unclear. Molecular dynamics experiments (14) have shown that defects analogous to a vacancy in a crystalline lattice are highly unstable. Spaepen (15) has consequently suggested that the defects must be of a more diffuse nature and can be considered as local sites where the short range order deviates from that of the "ideal" glass. Such a site may, though it is not a pre-requisite, have associated with it some excess free volume. During structural relaxation the number of such sites is reduced and the free volume redistributed. Since the removal of an individual site need not involve the anihilation of any excess free volume it is possible to have significant changes in physical properties with little or no change in density of the glass. In the present case we are concerned only with those defects that contribute to the elastic modulus of the glass. According to Weaire et al (16) these may be mobile regions of excess volume. As an approximation we can assume that the fractional change in Young's modulus is proportional to the fraction of such sites that have been annealed out, i.e. f in equations 1 to 4 above. The fully relaxed glass is represented by f = 1 and f = 0 corresponds to the hypothetical structure that would be obtained by quenching a liquid at infinite cooling rate. The term f_o can be viewed as a measure of the quenching efficiency during glass formation and the consequent deviation of the as-quenched glass from the "ideal" glass. Our data yields a value of $f_o = 0.45$. The activation energy αf

varies from 0.81 eV in the as-quenched state to 1.8 eV in the fully relaxed glass. This latter value is considerably lower than that for crystallisation of the same glass (17) indicating that structural relaxation involves no long range diffusion of atoms.

In conclusion, then, we have shown that the Young's modulus is a very sensitive monitor of both the relaxation and crystallisation of a metallic glass. Such measurements may provide a very quick and convenient means of establishing the as-quenched state of a glass in situations where, for example, it is desired to compare samples prepared at different times or under different conditions. An advantage of such measurements over others such as Curie temperature is that the glass does not have to be heated and therefore undergoes no relaxation during the measurement. Moreover they are applicable to both magnetic and non-magnetic glasses alike so long as a saturating field is applied in the former case. A disadvantage is that the non sensitivity of Young's modulus to various types of structural rearrangement prohibits separation of chemical and topological effects.

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FIGURE CAPTIONS

Fig 1. Change of reduced delay time during isothermal annealing of $Cu_{60}Zr_{40}$ glass. The error bars are smaller than the points.

Fig 2. Change in velocity and Youngs modulus during isothermal annealing of $Cu_{60}Zr_{40}$ glass. The dashed curves are from partially crystalline materials. The error bars are smaller than the points.

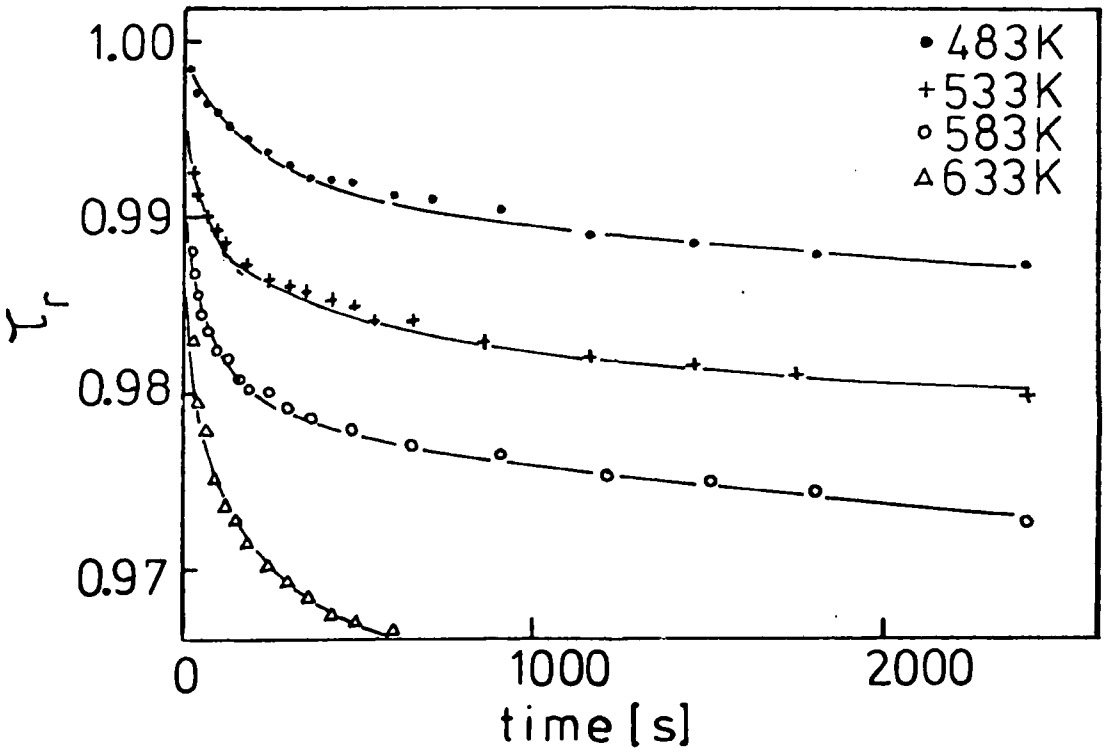

Fig 1

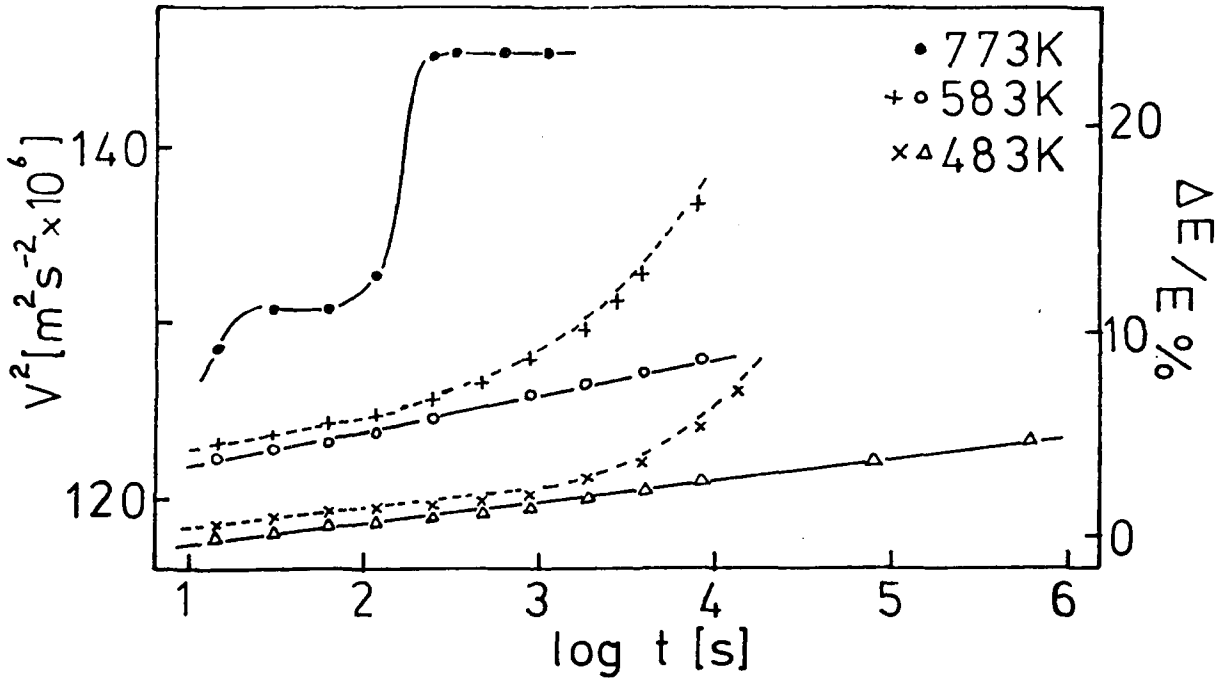
• 773K
+ ○ 583K
× △ 483K
V^2 [$m^2 s^{-2} \times 10^6$]
140
120
20
10
0
ΔE/E %
1
2
3
4
5
6
log t [s]

Fig. 2

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